Quality and authenticity of commercial aloe vera gel powders

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Abstract

This study provides a survey of commercial aloe vera gel powders. Nine products, obtained from leading international suppliers, were examined and compared with fresh aloe vera gel. A multi-technique approach was chosen to assess their quality and authenticity. Authenticity was evaluated by nuclear magnetic resonance spectrometry (^{1}H NMR). The absence of adulterants, impurities, and preservatives was also investigated by this technique. The amount of mannose after acid hydrolysis gave a direct and rapid measurement of the concentration of the polysaccharide acemannan in the gel powder. The quality of the samples analysed was found to be very inconsistent and in some cases extremely poor. Only three products, out of the nine analysed, contained satisfactory amounts of acemannan (ca. 10%, w/w) whereas the remaining samples exhibited very low levels. Two samples only contained ca. 1% (w/w). Four samples showed a high degree of enzymatic degradation and bacterial fermentation. One contained an abnormally high concentration of free glucose (ca. 30%, w/w). An HPLC–UV method was set up to verify the absence of hydroxyanthracene derivatives (aloin and aloin-related compounds). Aloin A was found to be present at concentrations from trace levels to ca. 16 mg/kg.

Keywords: Aloe vera gel powder; Authenticity; Quality; Acemannan; Aloin

1. Introduction

Aloe barbadensis Miller (aloe vera) is a perennial plant of the lily (Liliaceae) or Aloeaceae family. Since aloe has naturalised throughout the warm regions around the world, it is difficult to correctly establish its origin. It is supposed to be native of North Africa or the Nile region in Sudan. The genus *Aloe* contains over 400 different species with *Aloe barbadensis* Miller (aloe vera), *Aloe aborescens* and, *Aloe chinensis* being the most popular. *Aloe barbadensis* Miller is considered to be the most biologically active (Joshi, 1997; WHO, 1999; Yagi, Tsunoda, Egusa, Akasaki, & Tsuji, 1998).

The plant can be separated into two products: aloe latex and aloe gel. Aloe latex (or aloe juice) is the bitter yellow exudate from the pericyclic tubules in the outer skin of the leaves. The major and active constituents of aloe latex are hydroxyanthracene derivatives (15–40%) such as the anthraquinone glycosides aloin A and B (Saccu, Bogoni, & Procida, 2001). Aloe latex is known for its laxative properties.

Aloe gel is the colourless gel contained in the inner part of the fresh leaves (Reynolds & Dweck, 1999). The gel consists primarily of water (>98%) and polysaccharides (pectins, cellulose, hemicellulose, glucomannan, acemannan and mannose derivatives). Acemannan is considered the main functional component of aloe vera and is composed of a long chain of acetylated mannose (Djeraba & Quere, 2000; Femenia, Sanchez, Simal, & Rossello, 1999; Lee et al., 2001). Aloe gel is often commercialised as powdered concentrate. Traditionally, aloe vera gel is used both, topically (treatment of wounds, minor burns, and skin irritations) and internally to treat constipation, coughs, ulcers, diabete, headaches, arthritis, immune-system deficiencies (Eshun & He, 2004; Vogler & Ernst, 1999). The physiological activity of aloe vera polysaccharides has been widely

reported. Glucomannan and acemannan were proved to accelerate wound healing, activate macrophages, stimulate the immune system, and have antibacterial and antiviral effects (Davis, Kabbani, & Maro, 1987; Davis, Leitner, & Russo, 1988; Djeraba & Quere, 2000; Kaufman, Newman, & Wexler, 1989; Pugh, Ross, ElSohly, & Pasco, 2001; Tan & Vanitha, 2004; Visuthikosol, Chowchuen, Sukwanarat, Sriurairatana, & Boonpucknavig, 1995). Mannose-6-phosphate, a sugar constituent of aloe vera gel, was demonstrated to have wound healing properties (Davis, Donato, Hartman, & Haas, 1994). A number of glycoproteins present in aloe vera gel have been reported to have antitumor and antiulcer effects and to increase proliferation of normal human dermal cells (Choi et al., 2001; Yagi, Egusa, Arase, Tanabe, & Tsuji, 1997; Yagi et al., 2003). However, statistically significant clinical studies on the efficacy of aloe vera gel on human health are very limited and often inconclusive (Eshun & He, 2004).

Adulteration represents a major concern for the aloe vera market, mostly because of the high cost of the raw materials. Historically, the most common substance used to adulterate aloe gel powder is maltodextrin (Kim et al., 1998). Glucose, glycerine and malic acid have also been reported (Pelley, 1992; Pelley, Wang, & Waller, 1993). Many methods have been developed to detect adulteration and establish the authenticity of aloe gel powders. L-malic acid and some phenolic compounds (aloesin, barbaloin, and aloe-emodin) have been proposed as markers (Kim et al., 1998; Pelley, 1992; Pelley et al., 1993), although their concentration in aloe gel powders can vary significantly (due to normal biological variability) and depend on the manufacturing process. Carbohydrate analysis has also been considered. However, in this case only adulteration with sugars (i.e. glucose, sucrose) or polysaccharides (i.e. maltodextrin) could be revealed (Kim et al., 1998).

This study provides a survey of commercial aloe vera gel powders. Nine concentrates, obtained from leading international suppliers, were examined and compared with fresh aloe gel. ^{1}H NMR, profile of organic acids, profile of free sugars, and polymeric sugar analysis were used to assess authenticity and quality of the products. An HPLC-UV method was set up to verify the absence of hydroxyanthracene derivatives (aloin and aloin-related compounds).

2. Materials and methods

2.1. Materials

Formic acid (96%), fumaric, succinic, and tartaric acids (99%) were supplied by Sigma (Buchs, Switzerland). Acetic and citric acids (>99%) were Merck reagents (Darmstadt, Germany). Lactic and malic acids (>99%) were from Fluka (Buchs, Switzerland). Sodium hydroxide, 50% (w/w) aqueous solution, was purchased from J.T. Baker (NJ, USA). Sodium acetate anhydrous and carbohydrate standards were Fluka reagents (Fluka, Buchs, Switzerland). Acetonitrile was HPLC grade and supplied by Merck (Darmstadt, Germany). Aloin A (10-β-D-glucopyranosyl-1,8-dihydroxy-3-(hydroxymethyl)-9(10*H*)-anthracenone) of purity >97% from *Aloe barbadensis* Miller leaves, and standard Curaçao Aloe (aloe extract containing a minimum of 20% of aloin A) were purchased from Sigma (Buchs, Switzerland). Demineralised Milli-Q water (Millipore, MA, USA) was used to prepare samples, standards, and eluents.

2.2. Commercial aloe vera products analysed

Nine commercial powdered gel concentrates of aloe vera and one whole leaf extract, provided by leading international suppliers, were analysed and compared with aloe vera fresh gel (Table 1).

2.3. ^{1}H NMR of aloe vera gel powders

^{1}H NMR spectra at 300.13 MHz were recorder on a Bruker DPX-360 spectrometer, equipped with a 5 mm broadband multinuclear *z*-gradient (BBO) probehead. Powdered Aloe samples were dissolved in 0.7 ml of 99.9% deuterium oxide (Euriso-Top, France), and transferred in Schott Economic 5 mm NMR tubes. No internal shift standard was added.

Table 1
Commercial aloe vera samples analysed in this study

Sample name	Description	Comments
Reference	Fresh aloe vera gel dice	Frozen
Sample n.1	Concentrated gel powder (1:200)	Spray dried
Sample n.2	Concentrated gel powder (1:100)	Contains maltodextrin (declared additive)
Sample n.3	Concentrated gel powder (1:200)	Lyophilised
Sample n.4	Gel powder. Concentration not specified	Lyophilised
Sample n.5	Extract concentration not specified	–
Sample n.6	Concentrated gel powder (1:200)	Spray dried
Sample n.7	Concentrated gel Powder (1:200)	Spray dried
Sample n.8	Concentrated gel powder (1:200)	Freeze dried
Sample n.9	Concentrated gel powder (1:200)	Freeze dried and decolourised
Sample n.10	Whole leaf concentrated powder (1:100)	Freeze dried

2.4. Organic acid analysis

Acetic, citric, formic, fumaric, lactic, malic, succinic, and tartaric acids were analysed by HPLC–UV. Acids were extracted with water (30 min at 60 °C) and analysed on a cation-exchange HPLC column. The chromatographic system consisted of a Waters 2690 separation module and a Waters 996 photodiode array detector (Waters, MA, USA). Separation was carried out on a Nucleogel Ion 300 OA (300 × 7.8 mm) column equipped with a Nucleogel Ion 300 OA (21 × 4 mm) guard column (Machery-Nagel GmbH & Co. Düren, Germany). The mobile phase was H_2SO_4 4 mM and the flow rate 0.4 ml/min. The column was thermostated at 55 °C and the detector set at 210 nm. The volume injected was 20 µl.

2.5. Analysis of free sugars

Free sugars were analysed by high performance anion exchange chromatography with pulsed amperometric detection (HPAE-PAD). Water-soluble monosaccharides and disaccharides were extracted with water (30 min at 70 °C) and analysed on a Dionex DX500 ion chromatograph (Dionex, CA, USA). The system consisted of a GP40 gradient pump and an ED40 electrochemical detector equipped with a gold working electrode. Eluents were degassed with helium by a Dionex degas module. The samples and standard solutions were injected with an AS3500 Autosampler (Thermo Separation Products, USA) equipped with a 20 µl injection loop. Sugars were separated on an anion-exchange resin (CarboPac PA1 analytical column, 250 × 4 mm and CarboPac PA1 precolumn, 50 × 4 mm) using gradients of water (mobile phase A), NaOH 300 mM (mobile phase B), NaOH 150 mM/sodium acetate 500 mM (mobile phase C), and NaOH 100 mM (mobile phase D). The flow rate was 1 ml/min. Fructose, lactose, sucrose, and maltose were separated and quantified using the following gradient. *Acquisition*. Time 0 min = 65% A, 35% B; time 20 min = 55% A, 25% B, 20% C. *Clean-up*. 100% B for 10 min. Fucose, arabinose, rhamnose, galactose, glucose, xylose, mannose, and galacturonic, glucuronic and mannuronic acids were analysed using the following gradient. *Acquisition*. Time 0 min = 100% A; time 46 min = 52% A, 25% C, 23% D. *Clean-up*. 100% C for 15 min followed by 20 min with 100% B.

2.6. Monosaccharide analysis after hydrolysis

Aloe gel samples were hydrolysed with a two-steps acid hydrolysis. Pre-hydrolysis was carried out in H_2SO_4 12 M (30 °C, 1 h), then the hydrolysis was continued in H_2SO_4 0.414 M (130 °C, 75 min). The hydrolysed solutions were filtered through 0.2 µm membrane filters and quantified using the HPAE-PAD system already described. Fucose, arabinose, rhamnose, galactose, glucose, xylose, mannose, and uronic acids (galacturonic, glucuronic and mannuronic acids) were analysed using the same gradient already reported above.

2.7. Hydroxyanthracene derivatives in aloe vera

Hydroxyanthracene derivatives were analysed by high performance liquid chromatography (HPLC). The equipment used was the same as for organic acid analysis. The analytical column was a Lichrospher 100-5 RP-18, 250 × 4.6 mm (Machery-Nagel GmbH & Co. Düren, Germany). Hydroxyanthracene derivatives were extracted with methanol. Samples were sonicated in an ultrasonic bath for 10 min, filtered through 0.2 µm membrane filters, and 20 µl of solution analysed at a wavelength of 296 nm. The separation was carried out using acetonitrile (mobile phase A) and water/acetonitrile 90:10, v/v (mobile phase B). Acetic acid (0.1%, v/v) was added to mobile phase B to minimise peak tailing. The following gradient was used. *Acquisition*. Time 0 min = 5% A, 95% B (isocratic for 10 min); time 15 min = 15% A, 85% B (isocratic for 10 min); time 55 min = 22% A, 78% B; time 57 min = 5% A, 95% B. The flow rate was 1 ml/min.

All analyses were performed in duplicates. If the repeatability exceeded 5% of the arithmetic mean, the result was rejected and the measure repeated.

3. Results and discussion

3.1. ^1H NMR to assess identity and quality

Diehl and Teichmuller (1998) demonstrated that ^1H NMR was an essential tool to assess identity and quality of aloe vera gel preparations. Fig. 1 shows, as an example, the NMR spectra of two aloe vera gel concentrates of very different quality: (a) a gel powder concentrate 200:1 (sample n.8) and (b) a gel powder concentrate 100:1 (sample n.2). The signals corresponding to glucose, malic acid, and the polysaccharide acemannan, the three main natural components of aloe vera gel, are clearly present in the NMR spectrum of sample n.8 (Fig. 1(a)). Acemannan is a β-(1 → 4) linked mannan partially acetylated in positions 2, 3, or 6. In a ^1H NMR spectrum these acetyl groups generate a characteristic signal (2.00–2.26 ppm) that can be considered as the fingerprint of aloe vera (Diehl & Teichmuller, 1998). Conversely, in the NMR spectrum of sample n.2 (Fig. 1(b)) the signals revealing the presence of acemannan and malic acid are very low while the signal at 5.4 ppm indicates that the sample contains important amounts of maltodextrin. Although the presence of maltodextrin in this sample was indicated on the label, maltodextrin remains a common adulterant of aloe vera gel powders. Kim et al. (1998) carried out a survey of 21 commercial aloe gel powders and found that 33% of the samples examined contained high concentrations (45–95%, w/w) of undeclared maltodextrin.

The presence of some organic acids can also be deduced from the spectra in Fig. 1. The signal at 1.33 ppm indicates

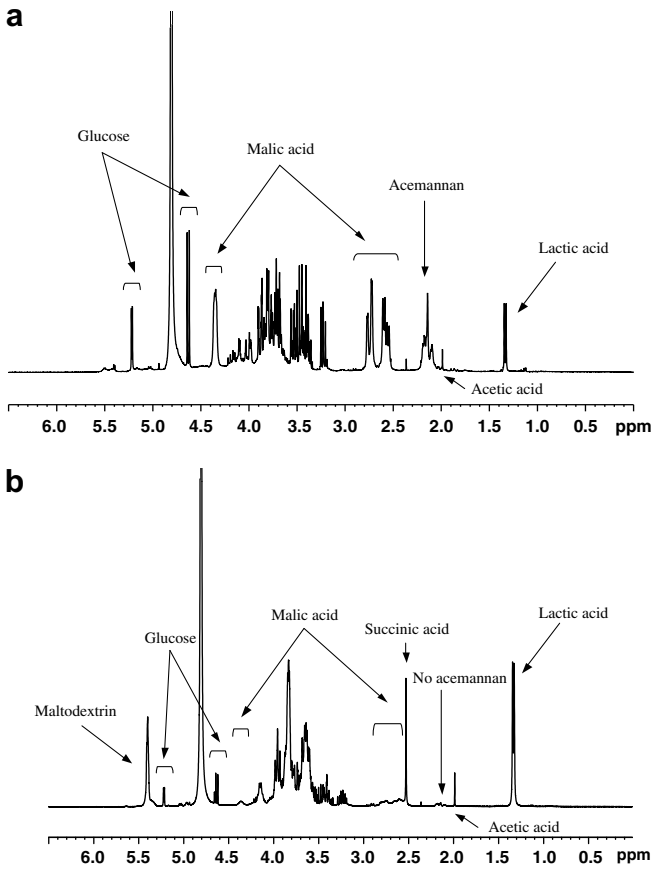


Fig. 1. ^{1}H NMR spectra of (a) aloe vera gel powder concentrate 200:1 (sample n.8) and (b) aloe vera gel powder 100:1 (sample n.2).

the presence of lactic acid. Significant amounts of acetic and succinic acids were also detected in sample n.2. Lactic acid, not a natural component of aloe vera, is the end product of *lactobacillus* fermentation. Therefore, high lactic acid content is a negative quality characteristic of aloe raw materials (Diehl & Teichmuller, 1998). Fumaric acid, succinic acid, and pyruvates may be produced by enzymes during the so-called citric acid cycle. The citric acid cycle should be interrupted after harvest because the photosynthesis is no longer possible. However, if an appropriate thermal treatment is not rapidly applied, a number of enzymes continue working, increasing the concentration of organic acids in the gel. In addition to fermentation and enzymatic degradation, chemical degradation can be initiated through improper processing or incorrect storage. During such chemical degradation acemannan is deacetylated resulting in the production of acetic acid. Among the nine aloe gel powders taken under consideration in this study, three were found to contain very low concentrations of acemannan (samples n.2, n.3, and n.4) and many showed an important degree of degradation. In particular: sample n.1 exhibited a very intense signal of lactic acid; in samples n.2 and n.3 lactic, succinic and acetic acids were present; and in sample n.5 the peak corresponding to acetic acid was quite noticeable.

3.2. Organic acid analysis to assess freshness

The concentration of organic acids was measured in the fresh gel (used as reference material) and in the nine commercial aloe vera gel powders (Table 2). The only organic acid contained in fresh aloe vera gel was malic acid. As previously mentioned, malic acid is a natural component of aloe gel and is essential for the plant photosynthesis as storage of carbon dioxide. Commercial aloe gel powders, on the contrary, contained important concentrations of organic acids other than malic. The most abundant were citric, lactic and succinic acids.

Citric acid is a natural preservative and is added to improve the flavour and to avoid oxidation. The pH of aloe vera gel juice is generally adjusted to 3.0–3.5 with citric acid before concentration and drying. Citric acid is widely used as an additive in the food industry. It is relatively cheap and safe. The maximum concentration of citric acid permitted in foods is quantum satis, i.e. unspecified, but not higher than that necessary to achieve the intended purpose (EU Regulation on Control of Additives for use in Foodstuffs, 1997). Nevertheless, the concentrations of citric acid measured in the samples were very inconsistent and certain samples were found to contain exceptionally high levels. Samples n.3, n.5, n.6, and n.7 contained more than 10 g/100 g of citric acid.

Lactic acid and succinic acid, as they are indicators of bacterial fermentation and enzymatic degradation, should be absent in a good quality aloe gel concentrate. However, four out of the nine products analysed contained more than 10% w/w of lactic acid (samples n.1, n.2, n.3, and n.9). The

Table 2
Concentration of organic acids (g/100 g) in commercial aloe vera gel powders and in the fresh gel (reference)

Acid	Reference	Sample n.1	Sample n.2	Sample n.3	Sample n.4	Sample n.5	Sample n.6	Sample n.7	Sample n.8	Sample n.9
Acetic	–	–	0.30	0.30	0.12	0.18	0.11	–	–	0.17
Citric	–	0.56	5.30	**10.30**	0.21	**14.19**	**16.17**	**13.88**	1.82	4.19
Formic	–	–	–	–	–	0.27	–	–	–	–
Fumaric	0.02	0.03	0.08	0.12	0.01	0.01	0.01	0.01	0.03	0.04
Lactic	–	**10.20**	**10.59**	**13.92**	–	0.13	0.04	0.92	1.43	**16.40**
Malic	20.20	19.32	4.26	17.57	35.74	19.60	30.98	22.40	29.78	2.58
Pyruvate	–	0.05	0.05	0.08	0.02	0.08	0.09	0.02	0.09	0.11
Succinic	–	1.04	**3.15**	**3.88**	0.39	1.39	0.47	0.90	0.78	0.85
Tartaric	–	–	–	–	–	–	–	–	–	–

Results for fresh aloe are expressed in g/100 g of dry matter (fresh aloe gel contains ~99% of water).

highest concentrations of succinic acid measured were 3.2 and 3.9 g/100 g in sample n.2 and sample n.3, respectively. The presence of acetic acid in some samples, even if at low concentrations, indicated that some chemical degradation had also occurred.

3.3. Free sugar analysis

In Table 3, the levels of free sugars measured in aloe gel powdered concentrates are reported and compared with the concentrations observed in the fresh gel. As foreseen, aloe vera fresh gel was found to mainly contain fructose and glucose (5.3 and 11.9 g/100 g of dry matter, respectively) in the ratio fructose:glucose of ca. 1:2. On the other hand, the concentrations of the same two sugars in the gel powder samples were quite variable and not always consistent. In at least four samples (samples n.2, n.3, n.4, and n.9), the concentration of free glucose was inexplicably high as compared to the concentration of free fructose. In particular, the powdered sample n.9 consisted of more than 28% (w/w) free glucose with a ratio fructose/glucose ca. 1:7. All the samples analysed contained low amounts of free mannose that is most probably generated from the degradation of the aloe polysaccharide acemannan. Samples n.2 and n.7 also contained some free galacturonic acid that might have been generated from the hydrolysis of pectins. During processing pectins are removed by pectinase enzyme in order to increase solubility. This would result in the production of free galacturonic acid. In sample n.2, which contains maltodextrin (Table 1), significant amounts of free maltose (1.1%, w/w) were detected.

3.4. Mannose after polysaccharide hydrolysis

Table 4 shows the amounts of monosaccharides released after hydrolysis of fresh aloe gel and aloe gel powders. For the fresh gel (reference), the major constituents of the cell wall polysaccharides were found to be glucose (19.6%, w/w), galacturonic acid (7.6%, w/w), mannose (3.9%, w/w), and galactose (1.4%, w/w). As previously reported (Femenia, Garcia-Pascual, Simal, & Rossello, 2003) aloe gel cell wall polysaccharides primarily consist of pectins, cellulose, and hemicelluloses. Pectins are in fact the main type of cell wall polysaccharides present in the aloe vera parenchyma.

Table 3
Concentration of free sugars (g/100 g) in commercial aloe vera gel powders and in the fresh gel

Sugar/acid	Reference	Sample n.1	Sample n.2	Sample n.3	Sample n.4	Sample n.5	Sample n.6	Sample n.7	Sample n.8	Sample n.9
Arabinose + rhamnose[a]	–	0.01	–	0.06	0.15	0.03	0.03	0.05	0.02	0.79
Fructose	5.30	4.33	0.56	3.61	1.72	5.86	3.23	9.62	5.02	3.95
Fucose	–	–	–	–	–	–	–	–	–	–
Galactose	0.05	0.08	0.06	0.15	0.12	0.17	0.09	0.13	0.11	0.20
Glucose	11.85	8.75	4.57	13.07	8.60	11.43	5.93	17.55	15.60	**28.27**
Lactose	–	–	–	–	–	–	–	–	–	–
Maltose	–	–	1.10	0.07	0.04	0.10	0.03	–	–	–
Mannose	0.08	0.13	0.03	0.19	0.10	0.17	0.04	0.15	0.13	0.19
Sucrose	0.16	0.18	0.87	–	–	–	1.46	0.51	1.45	–
Xylose	–	–	–	–	–	–	–	–	–	–
Galacturonic acid	–	–	3.07	–	0.08	–	–	1.92	0.14	0.30
Glucuronic acid	–	–	–	–	–	–	–	–	–	–
Mannuronic acid	–	–	1.43	–	–	–	–	–	–	–
Total	**17.4**	**13.5**	**11.7**	**17.2**	**10.8**	**17.8**	**10.8**	**29.9**	**22.5**	**33.7**

Results for fresh aloe (reference) are expressed in g/100 g of dry matter.
[a] Not fully separated in the chromatogram.

Table 4
Monosaccharides after acidic hydrolysis (g/100 g)

Sugar/acid	Reference	Sample n.1	Sample n.2	Sample n.3	Sample n.4	Sample n.5	Sample n.6	Sample n.7	Sample n.8	Sample n.9
Arabinose + Rhamnose[a]	0.78	0.19	0.08	0.13	0.17	0.17	0.12	0.15	0.17	0.18
Fucose	0.20	–	–	–	–	0.01	–	0.01	0.01	–
Galactose	1.44	0.46	0.18	0.35	0.30	0.51	0.27	0.30	0.38	0.36
Glucose	19.63	8.41	>40[b]	12.83	6.68	12.69	6.20	16.27	15.58	24.21
Mannose	3.87	9.84	1.42	1.30	2.17	3.19	4.20	4.74	11.06	10.54
Xylose	1.05	0.08	–	–	–	0.03	–	–	–	–
Galacturonic acid	7.55	0.03	–	0.05	0.16	0.03	0.09	1.06	0.85	0.23
Glucuronic acid	0.12	0.07	0.03	0.05	0.05	0.06	0.03	0.02	0.07	0.05
Mannuronic acid	0.06	0.06	0.08	–	–	0.06	–	0.04	–	–
Total	**34.7**	**19.1**	**47.6**	**14.7**	**9.5**	**16.8**	**10.9**	**22.6**	**28.1**	**35.6**

[a] Not fully separated in the chromatogram.
[b] This value is not to be taken as quantitative as the peak area was out of the instrument linearity range.

The presence of pectins can be deduced from the important amounts of galacturonic acid and galactose and from the occurrence of arabinose and rhamnose (Aspinall, 1980). Furthermore, the small amounts of xylose and fucose detected might indicate the presence of hemicellulosic xyloglucans (Aspinall, 1980). Some of the glucose could have been produced from the xyloglucan backbone with cellulose accounting for the rest. However, the most interesting bioactive aloe polysaccharide remains the acemannan fraction from which the mannose is derived. Acemannan should be the major polysaccharide present in aloe vera gel powders, as pectins and cellulose are generally eliminated during the processing.

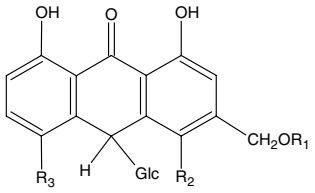
Ross, ElSohly, and Wilkins (1997) analysed 18 commercial samples of aloe vera products and found that only nine contained quantifiable amounts of aloe polysaccharides. In two samples, trace amounts were detected while seven samples contained no polysaccharides at all. Nevertheless, an appropriate concentration of aloe polysaccharides is an indispensable requirement for a concentrated gel powder of acceptable quality. The monosaccharide analysis of the nine gel powders showed, as expected, that the main monomer released after hydrolysis is mannose (Table 4). Sample n.8 was found to contain 11.1% (w/w) of mannose. This was the highest measured concentration. Samples n.1 and n.9 contained similar concentrations of mannose (9.8% and 10.5%, respectively) whereas the remaining samples exhibited inexplicably low levels, with samples n.2 and n.3 being the products of poorest quality (only 1.4% and 1.3% of mannose released by hydrolysis).

Femenia et al. (2003) measured the carbohydrate composition of isolated and purified acemannan from aloe vera parenchyma and found that mannose was the most abundant (82%) but not the only monomeric component of acemannan, which also contained galactose (4.5%) and glucose (10%). Small amounts of galactose were actually released during hydrolysis of aloe gel powders (Table 4). However, the glucose concentration after hydrolysis was in most cases not very different from the concentration measured before. The exceptionally high amount of glucose in sample n.2 (>40%, w/w) originated from the hydrolysis of maltodextrin.

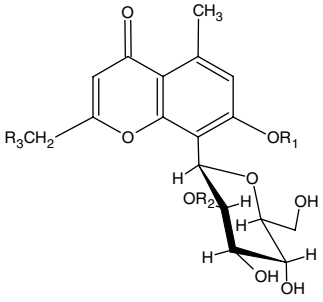
3.5. Determination of aloin and related phenolic compounds

Aloe latex (the bitter exudate from the outer skin of the aloe leaves) is widely used for manufacturing beverages, because of its aromatic properties and bitter taste, and pharmaceuticals for its laxative properties. The purgative activity, in particular, is due to some hydroxyanthracene derivatives abundantly present in it. The five main active principles are: the diastereoisomers aloin A and B (also named barbaloin), aloinoside A and B, and 5-hydroxyaloin (Fig. 2). Aloe latex may cause abdominal spasms and pain. Chronic use and excessive dose can lead to hepatitis. Long-term exposure may lead to electrolyte disturbances, metabolic acidosis, malabsorption, weight loss, albminuria and haematuria (WHO, 1999). These effects seem to be related to the presence of aloin, even though its mechanism of activity is not yet well understood. For this reason, the EU has fixed a maximum limit for the concentration of aloin allowed in foods and beverages (EEC Council directive 88/388). The maximum permitted concentration is 0.1 mg/kg with the exception of alcoholic beverages where the limit is set at 50 mg/kg.

An HPLC–UV method was set up to measure the concentration of aloin in aloe gel powder concentrates. The method allowed the simultaneous separation of several "aloin type" compounds. Considering that the concentration of these compounds is much higher in the aloe leaf skin than in the gel, whole leaf concentrates were used to optimise the elution. Fig. 3(a) shows the HPLC profiles of a standard aloe extract from Sigma (Curaçao Aloe) while the chromatogram of an aloe whole leaf extract (sample n.10) is reported in Fig. 3(b). As this profile was demonstrated to be typical of aloe (Kuzuya, Tamai, Beppu, Shimpo, & Chihara, 2001; Okamura, Asai, Hine, & Yagi, 1996; Saccu et al., 2001; Yamamoto, Ishikawa, Masui, Nakazawa, & Kabasawa, 1985; Zonta, Bogoni, Masotti, & Micali, 1995), the similarity between the two chromatograms indicates that sample n.10 is most probably an authentic aloe vera leaf extract. Aloin A (peak 5) was identified by using the available commercial standard. By com-



	R_1	R_2	R_3	Configuration C_{10}	Configuration C_1'
Aloin A	H	H	H	S	S
Aloin B	H	H	H	R	S
4-Hydrxyaloin	H	OH	H	-	-
5-Hydrxyaloin	H	H	OH	R	S
Aloinoside A	α-L-Rhamnosyl	H	H	S	S
Aloinoside B	α-L-Rhamnosyl	H	H	R	S



	R_1	R_2	R_3
Aloesin	H	H	$COCH_3$
Aloeresin A	H	p-Coumaroyl	$COCH_3$
8-C-glucosyl-7-O-methyl-(S)-aloesol	CH3	H	$CH(OH)CH_3$

Fig. 2. Molecular structure of some compounds typically present in aloe exudates.

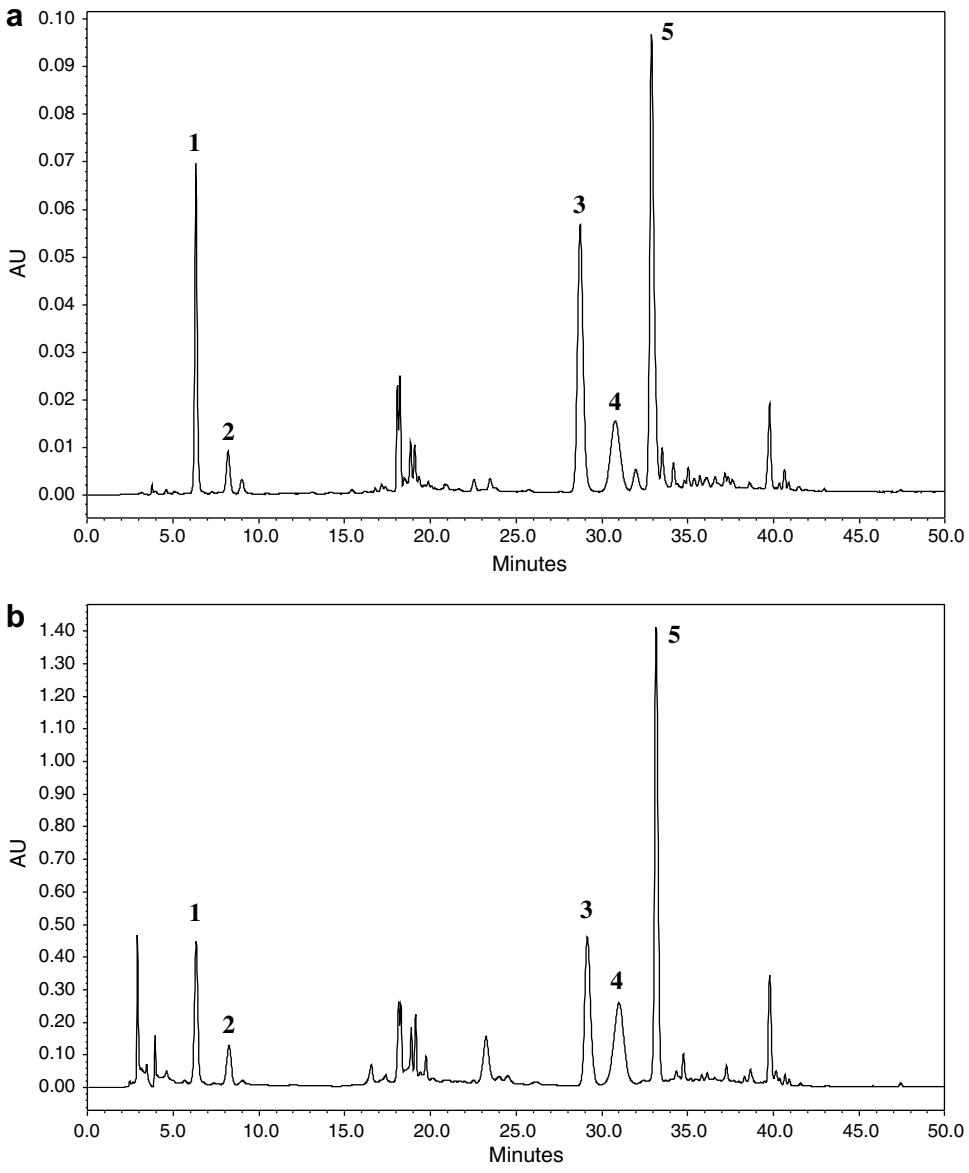


Fig. 3. HPLC–UV profile of (a) a standard aloe extract from Sigma (Curaçao Aloe) and (b) a whole leaf commercial aloe extract (sample 10). (1) Aloesin; (2) 8-*C*-glucosyl-7-*O*-methyl-(*S*)-aloesol; (3) aloin B; (4) aloeresin A; (5) aloin A. Detection wavelength: 296 nm; other chromatographic conditions as described in the text.

parison of the spectral data and the retention times with those in the literature, peaks 1, 3 and 4 were assigned to aloesin, aloin B, and aloeresin A, respectively. Peak 2 is probably 8-*C*-glucosyl-7-*O*-methyl-(*S*)-aloesol, a compound with a structure similar to aloesin whose presence in the extract from Sigma had been already reported (Saccu et al., 2001). This compound also appears in the chromatogram of the commercial leaf extract (sample n.10). The remaining eluting compounds were also phenolic derivatives characteristic of aloe vera as they all exhibited the typical absorption maxima at 295–300 nm and 354–360 nm (Kuzuya et al., 2001; Okamura et al., 1996; Saccu et al., 2001; Yamamoto et al., 1985; Zonta et al., 1995).

Aloe vera gel should not contain aloin or other hydroxyanthracene derivatives, as they are exclusively concentrated

Table 5
Concentration of aloin A in aloe vera gel powder samples (n.d.: not detected, n.a.: not analysed)

Aloe gel powder sample	Aloin A (mg/kg)
Sample n.1	0.7
Sample n.2	0.1
Sample n.3	n.d.
Sample n.4[a]	n.a.
Sample n.5	n.d.
Sample n.6	n.d.
Sample n.7	3.0
Sample n.8	15.9
Sample n.9	4.6
Sample n.10	0.7

[a] The analysis of aloins was not carried out on this sample because not enough material was available.

in the leaf skin. However, the mechanical separation process is not always complete, so some aloe latex can be found in the gel. Table 5 shows the concentration of aloin A in the aloe gel powders under consideration in this study. The concentrations reported have to be taken as indicative since the analytical method used was not fully validated. Most samples contained an equal amount of what was identified as aloin B. Sample n.8 contained the highest concentration of aloin A (15.9 mg/kg). However, these concentrates are generally added to food products or beverages at the maximum level of 0.1%. In this case, the aloin concentration is far below the regulatory limit for all samples analysed.

4. Conclusions

Nine powdered concentrates of aloe vera gel, obtained from leading international suppliers, were examined in this study and compared with fresh aloe vera gel. The essential components of the gel (acemannan, malic acid, and glucose) were identified by means of ^{1}H NMR. The profile of organic acids provided information about the freshness of the product and the time between the harvest and the processing. The amount of mannose released after acid hydrolysis was used to quantify the concentration of mannan in the gel powders. An HPLC–UV method was set up to verify the absence of hydroxyanthracene derivatives in gel powder concentrates.

The quality of the samples analysed was found to be quite inconsistent and in some cases very poor. Only three products contained satisfactory amounts of the polysaccharide acemannan (at least 10%, w/w) whereas in the remaining samples its concentration was very low (1–5%). Four samples contained more than 10% (w/w) of lactic acid, which indicates a high degree of bacterial fermentation. Two samples showed an important degree of enzymatic degradation, containing significant amounts (3–4%, w/w) of succinic acid. Five were found to contain low amounts of aloin A and B whereas in the remaining samples these compounds were not detected.

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